A RESEARCH STUDY ON INTERNAL CORROSION OF HIGH PRESSURE BOILERS

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SECOND PROGRESS REPORT

by

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ABSTRACT

The following report is the second in a series of three describing the progress of "A Research Study on Internal Corrosion of High Pressure Boilers." The first progress report, presented by Messrs. H. A. Klein and J. K. Rice at the 1965 annual meeting of the ASME, describes the background, scope, and organization of the program as well as the test facility.

This second progress report describes the results of the first half of the study. Results of tests with volatile, coordinated phosphate, and caustic boiler water treatment under conditions simulating a boiler with clean internal surfaces and one whose surfaces have been fouled with typical preboiler corrosion products, are included. Data relating to deposition and corrosion in the above environments are presented. The corrosion failure of a test tube due to "caustic gouging" and the discovery of an unusual effect of deposits on boiling characteristics are described.

INTRODUCTION

The first progress report of this series discussed the general background of this investigation, including the scope of the program, the philosophy of testing, and a detailed description of the test apparatus. The goals of the 4-phase test program are to reproduce and study, under controlled laboratory conditions, three of the most commonly experienced types of internal corrosion in steam generators. These are as follows:

1. Ductile gouging or pitting attack

2. Hydrogen damage or embrittlement

3. Plug type oxidation

Earlier work (Phase I) defined the most severe nucleate boiling conditions under which it would be possible to conduct the corrosion studies. A Steering Committee, representing the program's sponsors, selected the heat transfer parameters from Phase I data at which all twelve of the two-week tests were to be conducted (Phases II and III). It was intended that these short-term tests would produce the types of corrosion described above and that their results would be applied in the selection of variables for future long-term experiments (Phase IV) which would more closely simulate conditions representative of operating boilers.

Table I identifies the general experimental conditions for the Phase II and Phase III tests in terms of boiler water treatments and types of contaminants to be employed.

This second progress report includes the results of the six tests of Phases II and III-A which were designed to investigate boiler tube corrosion with each of the three methods of water treatment at conditions simulating

(1) a boiler with clean internal surfaces, and (2) a boiler whose internal surfaces have been fouled with typical preboiler corrosion products.

TEST EQUIPMENT

Combustion Engineering's heat transfer and corrosion test loop is illustrated in Fig. 1. This equipment was fully described in the first progress report, however, several modifications have been made to the loop as a result of test experience.

1. The original horizontal preheat furnace was replaced because its arrangement of external heat input in horizontal runs of large diameter tubing appeared to result in steam blanketing. The new preheater consists of a nest of smaller-diameter tubing, containing Inconel* immersion heaters. This equipment has proven satisfactory.

2. The original condenser configuration shown in Fig. 1 caused entrainment of hydrogen in the condensate. As a result, the steam vent was ineffective in reducing hydrogen concentrations and the high levels experienced interfered with interpretation of corrosion data. A reflux condenser was installed vertically on top of the drum to correct this problem. Non-condensibles collect at the top of this device, thereby permitting effective venting. The original condenser is still employed at partial load to obtain pressure control.

3. High colloidal silica concentrations in the raw water supply created a silica-control problem when make-up was prepared through a combina-

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TABLE I

PROGRAM ORGANIZATION

| Phase No.	Group	Test No.	Treatment	Boiler Condition	Boiler Water Contamination
II	—	1	Volatile	Clean	None
		2	Phosphate	Clean	None
		3	Caustic	Clean	None
III	A	1	Volatile	Dirty—Fe_3O_4 + Cu	None
		2	Phosphate	Dirty—Fe_3O_4 + Cu	None
		3	Caustic	Dirty—Fe_3O_4 + Cu	None
	B	1	Volatile	Dirty—Fe_3O_4 + Cu	Fresh Water Salts
		2	Phosphate	Dirty—Fe_3O_4 + Cu	Fresh Water Salts
		3	Caustic	Dirty—Fe_3O_4 + Cu	Fresh Water Salts
	C	1	Volatile	Dirty—Fe_3O_4 + Cu	Sea Water Salts
		2	Phosphate	Dirty—Fe_3O_4 + Cu	Sea Water Salts
		3	Caustic	Dirty—Fe_3O_4 + Cu	Sea Water Salts
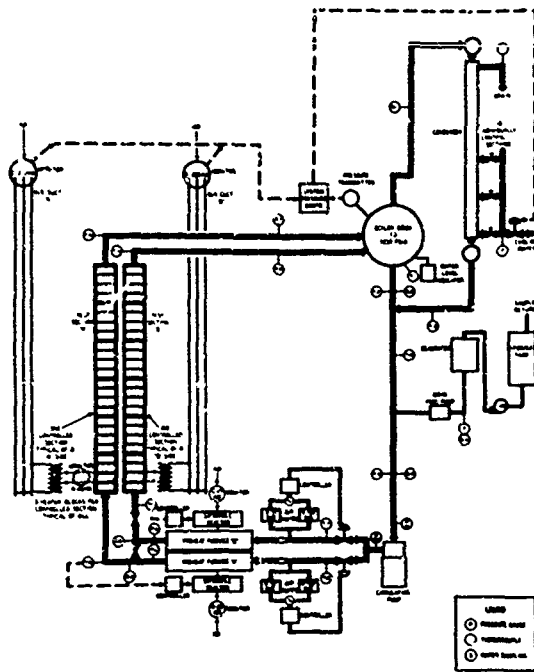
Fig. 1: *Schematic arrangement of the heat transfer and corrosion test loop*

tion of two-bed and mixed-bed demineralizers. The make-up system has since been modified to include (1) a two-bed demineralizer, (2) an evaporator, and (3) a mixed-bed demineralizer. Since this change, silica has not been a problem.

TEST CONDITIONS

1. *Test Sections*

Commercial, Type SA-192, carbon steel, boiler tubing was employed for all of the test-sections used in the program. Details relating to the composition and structure of this material are included in Appendix I '.

2. *Water Specifications*

Details relating to the three types of boiler water treatment, with which these tests were run, are listed in Table II. Specifications and analyses of the magnetite and metallic copper contaminants, used to simulate the deposits frequently found in boilers, are included in Appendix II.

3. *Heat Transfer Conditions*

The heat transfer conditions for these tests are summarized in Table III. Figures 2 and 3 show, schematically, the nominal conditions which existed in the A and B test loops, respectively.

PROCEDURE FOR EXAMINATION AND ANALYSIS

Subsequent to the completion of each test, test-sections were removed from the loop, vacuum dried, and then inspected using a borescope. Significant internal areas of the tube were often photographed through this device. Following inspection the test tubing was sectioned and the surfaces photographed. Deposits were then removed from various specimens by chemical cleaning and the metal surfaces were inspected and photographed.

Transverse sections were cut and mounted for microscopic and metallographic examination. Photomicrographs of both the deposits and metal structure were taken for future reference. Deposits were mechanically removed from both the heated and unheated
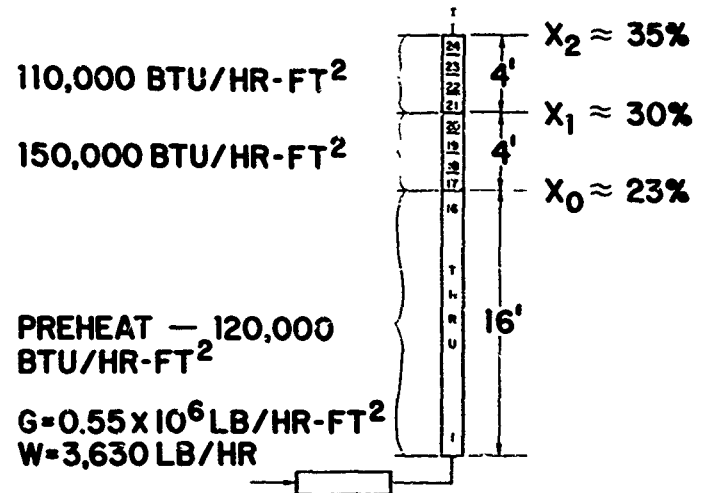

$110,000 \text{ BTU/HR-FT}^2$

$X_2 \approx 35\%$

$X_1 \approx 30\%$

$150,000 \text{ BTU/HR-FT}^2$

$X_0 \approx 23\%$

$\text{PREHEAT} - 120,000 \text{ BTU/HR-FT}^2$

$G = 0.55 \times 10^6 \text{ LB/HR-FT}^2$

$W = 3,630 \text{ LB/HR}$

Fig. 2: *Schematic diagram showing the "A" loop heat transfer and flow conditions*

TABLE II
WATER SPECIFICATIONS FOR 2600 PSIG

Name Treating Chemical	pH Value at 25 C	Hydroxide ppm OH	Phosphate ppm PO$_4$
VOLATILE (NH$_3$)	8.6—9.0	0	0
PHOSPHATE (Na$_3$PO$_4$)	9.8—10.0	0	9–11
CAUSTIC (NaOH)	10.5—10.7	AS REQUIRED TO MAINTAIN pH	2–4

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TABLE III

NOMINAL TEST CONDITIONS

NOMINAL TEST CONDITION	A	B
Mass Velocity (G) = lb/hr-ft²	0.55×10^6	0.55×10^6
Flow Rate (W) = lb/hr	3,630	3,630
*Heat Flux $(Q/A)_1$ = Btu/hr-ft² (based on ID of tube)	150,000	150,000
Heat Flux $(Q/A)_1$ = Btu/hr-ft² (based on projected area)	173,000	173,000
**Heat Flux $(Q/A)_2$ = Btu/hr-ft² (based on ID of tube)	110,000	110,000
Heat Flux $(Q/A)_2$ = Btu/hr-ft² (based on projected area)	127,000	127,000
Approx. Total Preheat (Q) = Btu/hr	280,000	97,000
***Approx. Preheat Flux (Q/A) = Btu/hr-ft²	121,500	42,000
Approx. Quality (X_0) Entering Test Section	23%	8%
Approx. Quality X_1 Leaving $(Q/A)_1$	30%	15%
Approx. Quality X_2 Leaving $(Q/A)_2$	35%	20%

*$(Q/A)_1$ Heat flux in lower test section
**$(Q/A)_2$ Heat flux in upper test section
***These fluxes are based on the entire 16 feet of vertical preheat

surfaces, weighed, and submitted for spectrographic, x-ray, and ultimately wet chemical analysis.

Typical results obtained from the examinations and analyses described above are included with the individual test summaries in Appendices IV through IX.
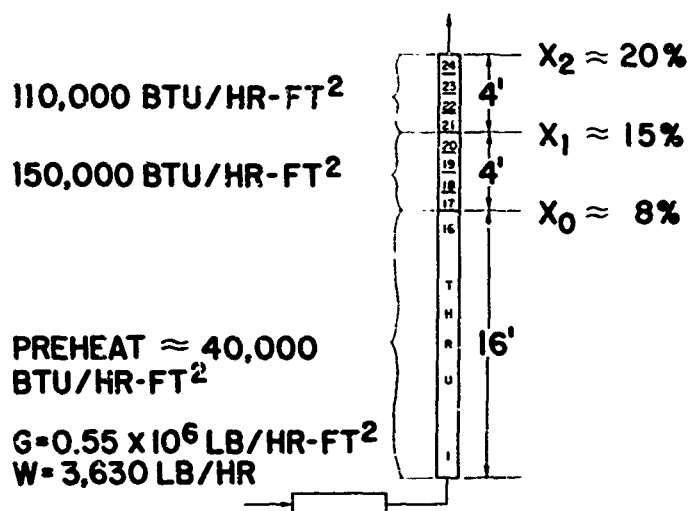

Fig. 3: Schematic diagram showing the "B" loop heat transfer and flow conditions

DISCUSSION OF RESULTS

The results are divided into four sections, each of which includes observations from all six tests. Each section is, however, restricted to a specific subject area. These subjects are: (1) deposits, (2) corrosion, (3) phosphate hideout, and (4) effects on heat transfer.

Throughout this discussion, reference is made to "clean boiler" and "dirty boiler" tests. These terms were adopted to describe, respectively, the groups of tests run with contaminant-free boiler water (Phase II) and those where iron-oxide and metallic-copper contaminants were introduced (Phase III-A).

In order to obtain the greatest assurance of visible effects in the relatively short test periods, severe combinations of local heat absorption and mixture quality were selected. In evaluating the following results, it should therefore, be kept in mind that the conditions employed were intended to accelerate corrosion rather than to duplicate typical boiler operation.

1. *Deposits*

Although considerable amounts of contaminants were added during dirty-boiler tests, a large percentage of these materials deposited in the relatively large drum and other areas of the test loop. This discussion, however, only refers to the deposits found on the test-section, heat-transfer surfaces.

The data collected from the clean-boiler and dirty-boiler tests respectively, reveal consistent trends in the distribution of deposits with relation to heat flux and quality. Figures 4 and 5 illustrate the typical distribution among the various portions of the A and B test sections. The values listed are average deposit weight per linear foot as removed from the heated side of tubing. Data in Fig. 4 indicate the maximum accumulation of deposit in the high-heat-flux section of the A loop. This area and the lower-heat-flux section of the same loop both accumulated more material than the surfaces of the high-heat-flux zone of the B test section. Figure 5 breaks down the distribution of deposit in a high-heat-flux section, revealing an increase in quantity of deposit with mixture quality. The deposits referred to in Figs. 4 and 5 were primarily composed of contaminant materials. These results indicate that deposition of suspended magnetite and metallic copper increased with both increasing heat flux and mixture quality.
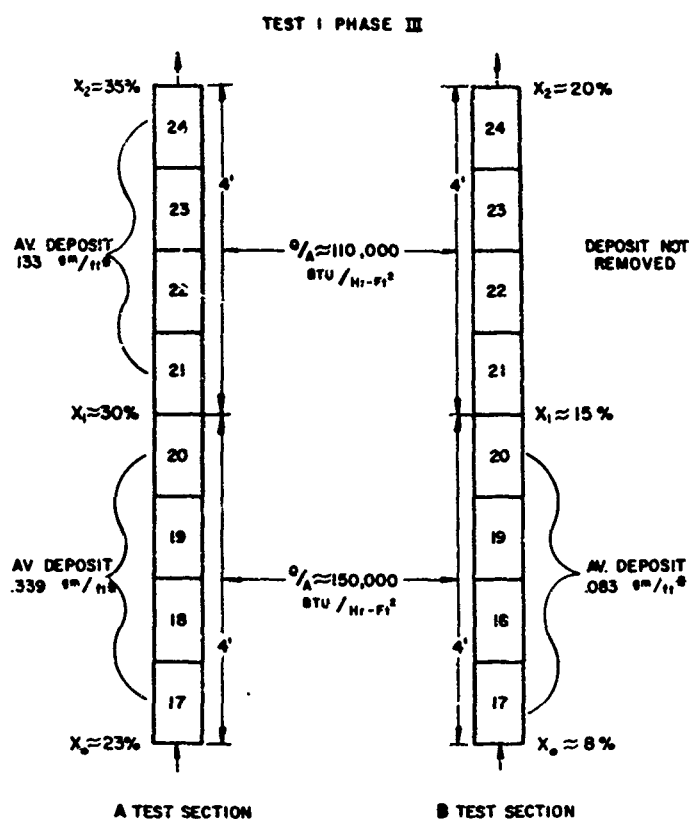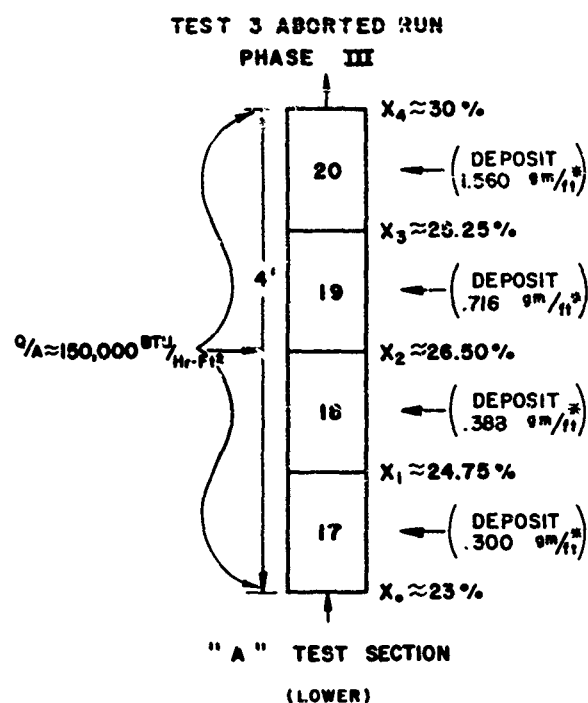
Fig. 4: Typical deposit distribution of both the "A" and "B" test sections

Fig. 5: Typical deposit distribution on a high-heat-flux "A" loop test section

* GRAMS PER LINEAR FOOT OF HEATED SIDE SURFACE
X = MIXTURE QUALITY — % STEAM BY WEIGHT

TABLE IV
DEPOSIT CHARACTERISTICS

	Phase II			Phase III		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Thickness, mils	<0.5	<0.5	<0.5	4.0	3.0	93.0
Avg. weight per linear foot of 1½" tubing— heated side, gm/ft.	0.077	0.148	0.086	0.327	0.310	0.988
Tube crown temp. rise max, F	0	0	0	7	0	78
Composition						
% Fe as Fe_3O_4	Major	Major	Major	46–63	94	64–89
% Cu as Cu	—	—	—	16–30	1	10–20
% Si as SiO_2	—	—	—	9–16	0.5	1
Other significant constituents— >1%	None	PO_4	None	Ca, Al	None	Na, PO_4, CO_3
Mixture quality for DNB at block 20—% steam by weight						
(a) Clean tube	39	39	39	39	39	39
(b) Min. with deposit	—	—	—	33	34	32.5

The amount, effect, and composition of the deposits removed from the test surfaces of six runs are included in Table IV. Less than 0.5 mils of deposit was found on the surfaces from the clean-boiler tests. Analyses and examinations of these materials showed them to be mostly magnetite which had formed in place. No tube-crown temperature elevation was noted during these first tests.

Although comparable amounts of iron oxide and metallic copper were added to the loop during
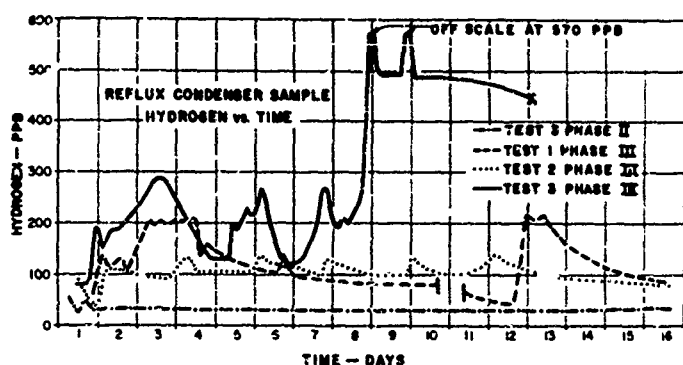
Fig. 6: Comparative plot of hydrogen evolution data from 1 "clean boiler" and 3 "dirty boiler" tests

the three dirty-boiler tests, some interesting differences in both the quantity and composition of the deposits formed may be seen in Table IV.

The ammonia run resulted in a deposit containing appreciable amounts of amorphous silica. Virtually no silica was found in the deposit from either the phosphate or caustic tests. It is also interesting that considerable amounts of particulate copper metal were found in the deposits from the volatile and caustic runs, with virtually none present in those from the phosphate test. The silica present in the volatile-run deposit produced a relatively dense and adherent material. In contrast, the deposits formed in the phosphate run were porous and show evidence of flaking loose. Caustic treatment allowed the rapid build-up of a heavy, but extremely porous deposit made up of contaminant materials as indicated by the results of the aborted test. (Deposit photographs are included in the Appendix.)

The dirty-boiler phosphate test produced no detectable tube-crown temperature rise in spite of significant contaminant addition to the loop. The volatile test produced a maximum increase of approximately 7 F, with roughly the same level of contaminant introduced, while an increase of as much as 78 F was experienced during the caustic run.

These results indicate that deposition is greater on heat-transfer surfaces with caustic treatment than with either of the other environments. Each of these three treatments demonstrated additional differences related to deposition as shown by variations in composition of the deposits produced.

2. Corrosion

Analysis of the operating data and the appearance of test specimens reveal that no significant cor-

rosion occurred during the three clean-boiler tests. Calculated rates of corrosion of heat transfer surfaces, based upon hydrogen-evolution data, were less than one mil per year.

Only minor traces of corrosion occurred on test sections with volatile and phosphate treatment during the dirty-boiler runs. In both cases a narrow band of wastage, estimated at not more than 0.1 mils, was noted on the tube crown of the high-heat-flux section. This, however, was not the case where caustic treatment was employed. After eleven days of operation, almost total corrosion penetration (150 mils) of the test section had occurred and a resulting tube failure ended this
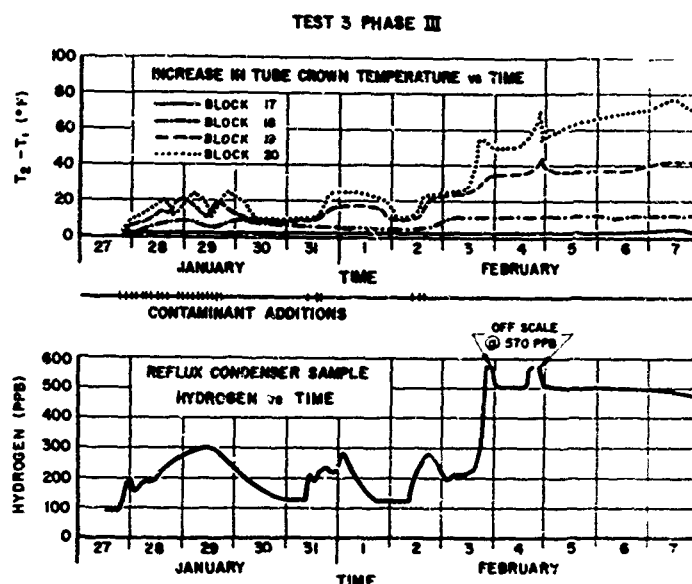

Fig. 7: Plot of tube-crown-temperature and hydrogen evolution data from the "dirty boiler" caustic test

test. Hydrogen-evolution data, comparing these three dirty-boiler runs and the clean-boiler caustic test, are shown by Fig. 6.

Figure 7 shows the relationship between hydrogen evolution and the deposit effect upon tube crown temperature during the dirty-boiler caustic run. This plot reveals that the initial increases in temperature and hydrogen were triggered by contaminant additions, but that later in the test self-sustaining increases in both values occurred. Photographs of the ruptured tube and the damaged test loop are shown in Figs. 8 and 9.

The two curves, shown in Fig. 10, compare the temperature rise and hydrogen evolution of the completed run with the results of an aborted run with the same water environment and degree of surface fouling. It is significant that both curves reveal a similarity of response to contaminant addition in both rate of increase and

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Fig. 8: Photograph of a corrosion failure resulting from caustic gouging during the "dirty boiler" caustic test

peak levels of tube-crown temperature and hydrogen evolution. These data indicate initial hydrogen levels as much as 35 percent higher than those reached during similar periods of the volatile and phosphate dirty-boiler tests. Examination of the aborted-run high-heat-flux test section revealed that pits as much as 2 mils deep had formed during 36 hours of operation.

It is interesting to note that corrosion appeared to occur in the horizontal preheater during the clean-boiler caustic test. In this case, the attack probably occurred as a result of steam blanketing in this low-velocity horizontal run of tubing. Figure 11 shows the corroded surface.

Metallurgical examination of specimens from each of the six runs revealed that no changes in metal structure had occurred.

3. *Phosphate Hideout*

Data on phosphate hideout was gathered during shutdown at the conclusion of the phosphate tests. No hideout was observed in either the test sections or vertical-preheat areas following the clean-boiler run. However, a considerable increase in the phosphate concentration was noted after shut-down of the horizontal preheater. The results of a similar check at the end of the dirty-boiler test revealed hideout, primarily in the high-heat-flux portion of the A-loop, as shown by Fig. 12. No increase in suspended matter was noted in the boiler water during these tests.

These data suggest a relationship between deposition and phosphate hideout. It is likely that phosphate precipitated within the porous deposits in the dirty-boiler run as a result of a concentrated film and the limited solubility of

sodium phosphates at the test temperature. This material redissolved in the boiler water when the heat input was eliminated. Steam blanketing was probably responsible for the hideout experienced in the original horizontal preheater during the clean-boiler run. The modified preheater employed during the dirty-boiler tests apparently does not experience this problem.

4. *Effects on Heat Transfer*

The test data indicate that deposition on internal tube surfaces can have an effect on the characteristics of boiling heat transfer. Deposits can apparently induce DNB under conditions where nucleate boiling would exist if the tube surfaces were clean.

The term DNB (Departure from Nucleate Boiling) describes the region of boiling heat transfer beyond the conditions of stable nucleate boiling. Generally speaking, this includes both the unstable transitional-boiling zone and the stable film-boiling region. In this discussion, DNB refers to the threshold of the transitional-boiling region.

The significant parameters relating to DNB are pressure, mass velocity, heat flux, and mixture quality. These parameters are frequently

Fig. 9: Photograph showing the damaged test loop after the corrosion failure
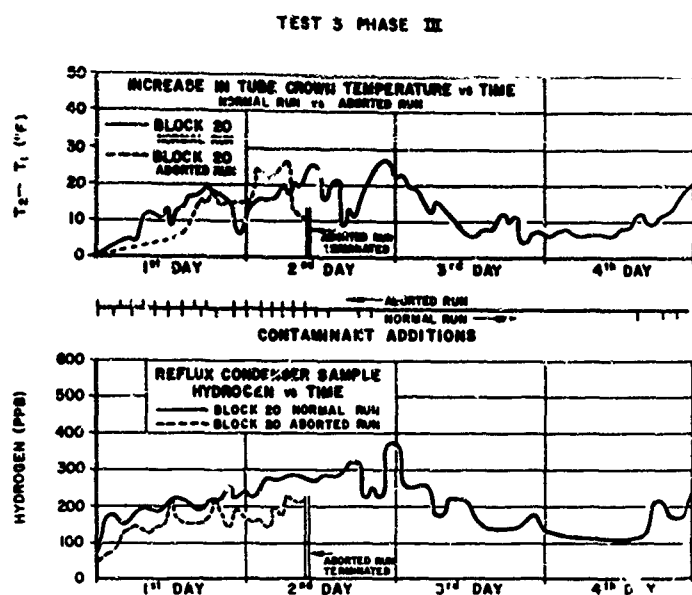
Fig. 10: *Comparative plot of tube crown temperature and hydrogen evolution from the aborted and completed "dirty boiler" caustic runs*

termed critical at the DNB point, i.e. critical flux, critical quality, etc. In these investigations, reference will be made primarily to critical quality since the configuration of the test loop allows us to conduct DNB tests by increasing quality without changing the other parameters. Test data has shown that with clean tube conditions DNB is a completely reproducible phenomenon. The critical quality is, however, determined with clean tube conditions at the beginning of each test. This is done to insure that the test conditions will be set as close to critical as possible. Test specifications call for operation at 5 percent quality below critical, which is the maximum possible if excursions into DNB due to inherent line-voltage variations are to be avoided.

In conducting the dirty-boiler tests, it was found that the deposition of contaminants on heat transfer surfaces resulted in a critical quality lower than that for a clean tube. This was first discovered during the volatile treatment run when DNB occurred at normal operating quality after only a few injections of contaminant. During the three dirty-boiler runs, periodic DNB tests revealed that the initial deposition of contaminants depressed the critical quality to approximately 33 percent. Subsequently, values returned to approximately the 39 percent clean-tube level. Periodic injections of contaminant at various times during each run also depressed the critical quality followed by subsequent increases. The return to clean-tube levels often occurred within a few hours. This effect was observed con-

currently with the various rates of tube-temperature increase of the three dirty-boiler tests.
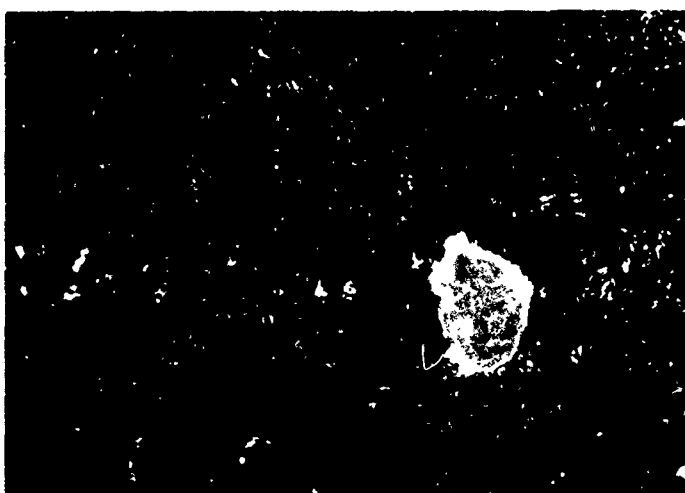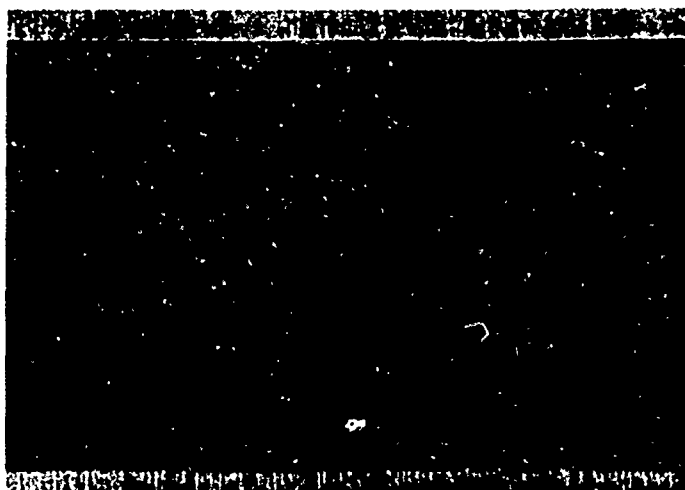
Fig. 11: *Upper—View of old horizontal preheat furnace 3-in. tubing showing area of corrosion*

Lower—Close up of corrosion pits
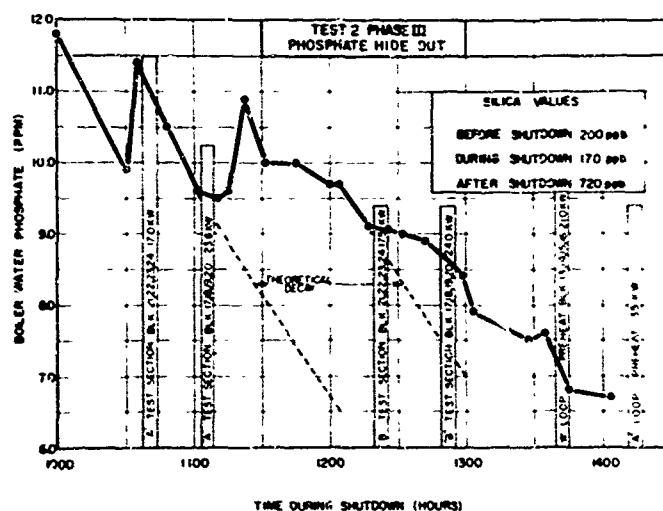
Fig. 12: *Results of a check for phosphate hideout after the "dirty boiler" coordinated phosphate test*

INTERIM CONCLUSIONS

Based upon the results of the six tests discussed, the following conclusions have been made:

1. In spite of the severe combination of high heat flux and mixture quality, no corrosion occurred with any of the three methods of boiler water treatment tested when the tube surfaces were clean.

2. Deposition of contaminants occurred almost exclusively on the heated portions of the test surfaces.

3. Deposition of contaminants was consistently greater in the A-loop (23 to 35 percent quality) than in the B-loop (8 to 20 percent quality). With the exception of quality, conditions in the 2 loops were identical with respect to heat flux, mass velocity, and pressure.

4. Within each test section the deposition of contaminants was greater in the high-heat-flux zone (blocks 17-20) than in the lower-heat-flux area (blocks 21-24).

5. Within a 4 block test section deposition of contaminants increased with quality at constant heat flux (i. e., block 20>19>18>17 and block 24>23>22>21).

6. Volatile treatment (pH 8.6 to 9.0) permitted the deposition of significant quantities of amorphous silica. Virtually no silica (<1 percent) deposited during the higher pH coordinated phosphate or caustic tests.

7. Volatile and caustic treatment permitted the deposition of substantial amounts of metallic copper particles; however, no copper was found in the deposits on heat transfer surfaces of the phosphate test.

8. When either volatile or phosphate treatment was used in a dirty boiler environment, no significant corrosion occurred.

9. The combination of fouled tube surfaces and caustic-base boiler water treatment caused high rates of corrosion under nucleate-boiling conditions.

10. The initial deposition of contaminants on tube surfaces initiated the caustic attack. Subsequent formation of additional deposits resulting from corrosion of the steel, sustained and finally accelerated the corrosion rate.

11. The absence of corrosion during the clean-boiler caustic test and the severe attack experienced during the dirty-boiler caustic test reveal that with deposit free surfaces, the rate of diffusion from the internal film to the bulk stream is sufficient to limit the equilibrium concentration to a value which will not destroy the protective oxide film. With the introduction of a porous deposit on the heated surface, transport of the solute is restricted, allowing caustic concentrations to more nearly approach those calculated for non-boiling equilibrium.

12. Porous deposits on heat transfer surfaces depressed critical conditions (quality, heat flux, mass velocity, and pressure) and resulted in DNB where nucleate boiling would have been experienced with clean test surfaces. This effect was temporary as indicated by increasing values of critical quality during a period of several hours subsequent to the addition to contaminants.

APPENDIX I
TEST PROCEDURE

Start-up of the test rig is begun with the loop entirely full of chemically treated, deaerated water under nitrogen pressure. Upon startup, horizontal-preheat sections are placed in operation with the loop vent open. As pressure is built up, the drum level is allowed to fall to its normal operating point. During this period, water chemistry is regulated in order to achieve the specified conditions as soon as possible. Once operating pressure (2600 psia) is reached, the loop is placed on automatic-pressure control. Flow through the A and B test loops is maintained substantially above operating values throughout start-up.

The vertical preheat sections for these loops are then placed in operation and adjusted, as is the horizontal preheater, to obtain the desired preheat input. The test sections are next placed in operation and power to the test sections is slowly increased until the specified heat-flux levels are reached. Having established the heat input and test section heat flux, circulating flow is reduced to the desired operating value and the loop is allowed to run at steady-state conditions until a constant hydrogen value is obtained. Once this steady-state value has been determined, the test is considered to have begun.

The following fourteen days of operation actually constitute a test. At least two operators are assigned to the loop each shift to assure continuity of operation and to permit collection of data and maintenance of specifications. Dirty-boiler tests require introduction of contaminants to the loop initially and intermittently during the period of operation; however, these tests are similar in all other respects to those simulating a clean boiler.

Shutdown procedures were established so that data could be collected to determine the location of areas of corrosion and phosphate hideout. The procedure used consists of removing of the uppermost portion of the A-loop test section from service followed by the lower A-loop test section. The same sequence is then repeated with the B-loop. A similar operation is carried out with the preheaters up to the point that pressure can no longer be controlled. At this time, the remaining power is cut and the loop is allowed to cool to approximately 300 F while maintaining operational flow rates. At this time the loop is drained. By using this procedure, starting at the top section and working downward, only that portion where the power is cut is affected. Hence, the contribution of phosphate and hydrogen to the system by the various areas of the loop can readily be established.

APPENDIX II
CONTAMINANTS USED FOR DIRTY-BOILER TESTS

Magnetic iron oxide and metallic copper powder were used as contaminants in creating dirty-boiler conditions for the Phase III tests. These were primarily selected because it was the intent of the program to study the effects of boiler water chemistry on dirty tube surfaces and these materials were known to redeposit from suspension in operating units.

It was recognized that other forms of iron and copper enter operating boilers, but the introduction of any material which would experience a chemical change in forming magnetite and metallic copper within the test loop would complicate the evaluation of test results. The use of materials removed from the drums of operating units was also given consideration; however, analysis of the deposits received from various utility companies revealed that although the primary constituents were magnetite and copper, the variations in particle size were excessive for our use.

Various vendors were contacted to obtain suitable material. Magnetic iron oxide, obtained from Fisher Scientific Company, was found to be the most suitable for our needs. Various analyses were performed on these materials to determine their purity. Gravimetric analysis by hydrogen reduction of the Fe_3O_4 revealed it to be 97 percent stoichiometric Fe_3O_4. Spectrographic analysis showed the presence of only minor traces of impurities and X-ray diffraction could detect no significant lines other than those of Fe_3O_4.

Metallic copper powder was obtained from Matheson, Coleman & Bell. Similar analyses of the copper used in these tests revealed the material to be 98.7 percent copper metal. Spectrographic analysis showed only minor traces of other constituents and X-ray diffraction revealed only copper lines.

Test Tubing Specifications

Type—SA-192, Hot Finish Carbon Steel
Size—1.5-in. OD, 0.200-in. MW
Composition: Carbon—0.06 to 0.18 percent
Manganese—0.27 to 0.63 percent
Phosphorous—0.48 percent maximum
Sulfur—0.58 percent maximum
Silica—0.25 percent maximum

The accompanying photomicrographs (Fig. III-1 and III-2) show the structure of the tubing material used for these tests at both 100 and 500 times magnification in the "as received" condition, and after heat treatment received in the brazing operation.

The first pair of photomicrographs (Fig. III-1) reveal that this tubing is received in a spheroidized condition. No changes in microstructure result from the nickel plating operation. Brazing at 1600 F and slow cooling over a 48-hour period yield a pearlitic microstructure as shown in the second pair of photomicrographs (Fig. III-2).
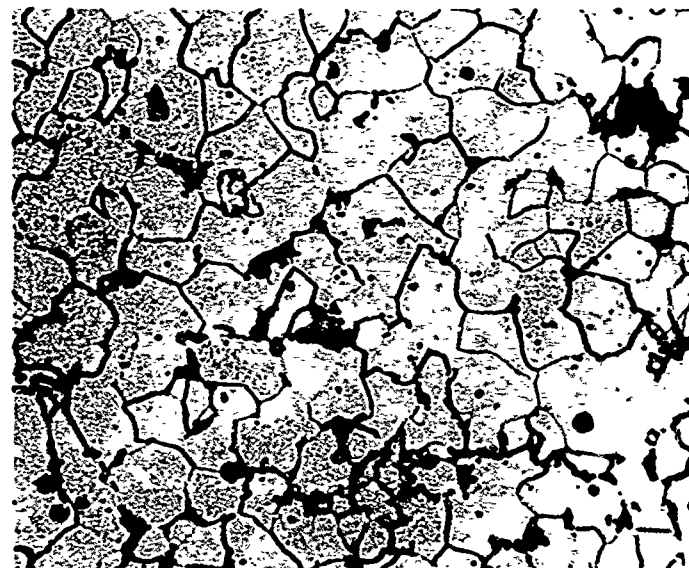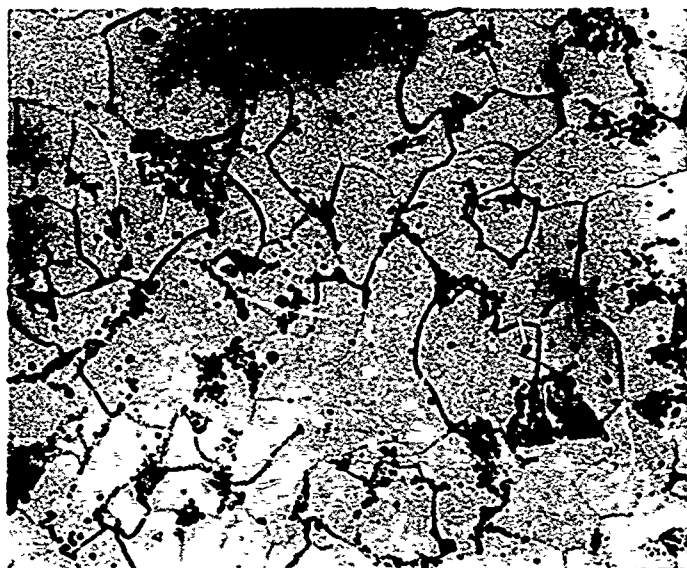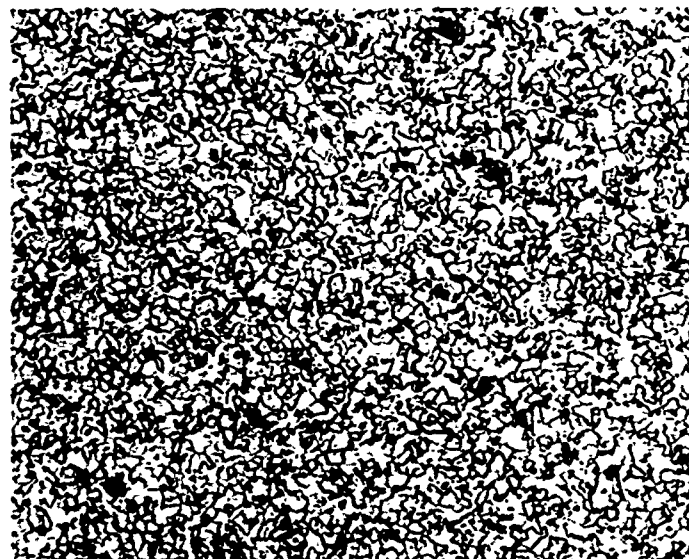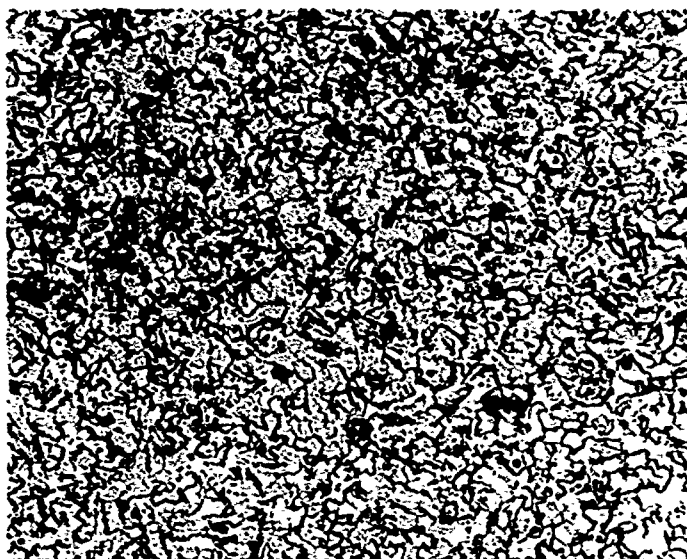

Fig. III-1: Upper—100x photomicrograph of "as received" SA-192 tubing showing spheroidized structure
Lower—500x photomicrograph as above

Fig. III-2: Upper—100x photomicrograph of SA-192 tubing after heat treament showing pearlitic structure
Lower—500x photomicrograph as above

APPENDIX IV

Log—Test 1, Phase II

Volatile (NH₃) Boiler Water Treatment
pH = 8.6 to 9.0
Clean Boiler Conditions

Boiler water chemistry was maintained within specified limits throughout most of the run. However, high silica levels occurred as a result of colloidal silica in the demineralized make-up water (Figs. IV-1 and IV-2). Excessively high levels of hydrogen in the steam persisted for several days after start-up despite attempts to blow down (Fig. IV-3). Analysis of samples from various locations showed that hydrogen was being entrained and recirculated in the condensate. This impeded the rejection of hydrogen from the loop.

Steady-state hydrogen data, obtained at the end of the test, indicated a heated-surface-corrosion rate of less than 1 mil per year. Inspection of the test surfaces revealed that the tubing was coated with an iron oxide film and that no detectable corrosion had occurred. Borescope examination revealed a similar surface appearance of the entire test section. For this reason, only the 110,000 Btu/hr-ft² portions were cut up. This was true of all the clean-boiler tests. Table IV-1 shows the quantity and analysis of the deposit film. No changes in metal structure were found.

TABLE IV-1

TEST 1—PHASE II
(Volatile Treatment—Clean Boiler)

DEPOSIT DISTRIBUTION

Loop	Q/A-Btu/hr-ft²	Heated/Unheated Side	Block Location	Gm/Linear Ft.
A	110,000	Unheated	24	0.036
A	110,000	Unheated	23	0.039
A	110,000	Unheated	22	0.042
A	110,000	Heated	24	0.084
A	110,000	Heated	23	0.083
A	110,000	Heated	22	0.065
B	110,000	Unheated	22, 23, 24	0.011
B	110,000	Heated	24	0.033
B	110,000	Heated	23	0.046
B	110,000	Heated	22	0.052

DEPOSIT ANALYSIS

X-ray Diffraction	Major, >30%—Fe₃O₄
	Minor, 8 to 15%—Fe₂O₃
	Trace, None
Spectrography	Major, >15%—Fe
	Minor, None
	Trace, 0.1 to 1.0%—Ni, Mn, Si, Cr, Mg, Al, Cu, As
Wet Chemistry	Na₂O—0.4%
	P₂O₅— <1.0%

PHASE II – TEST I, 1/25/65–2/7/65
BOILERWATER CHEMISTRY

NOTE:
ALL DATA FROM S-9
SAMPLE (FLOWRATE
8 GPH)

NOTE:
1. DATA FOR 8th DAY 0400
   TO 10th DAY 1900 SAMPLE
2. POINT S-2
   ALL OTHER DATA FROM
   S-9 SAMPLE (S-9 & S-2 FLOW
   -RATE 8GPH)
3. % TIME ON SPEC. 97 %

Fig. IV-1

PHASE II TEST 1
1/25/65 – 2/7/65
BOILERWATER CONDUCTIVITY

NOTE:
DATA FROM 8th DAY 1000
TO 10th DAY 1800 FROM
S-2 SAMPLE, ALL OTHER
DATA FROM S-9 SAMPLE
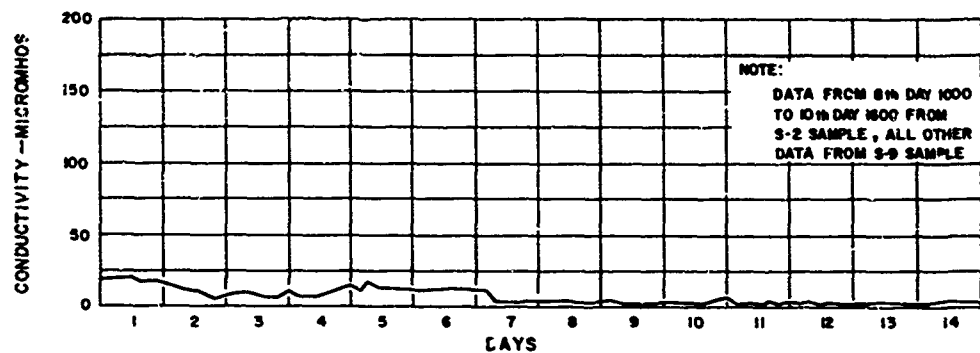
Fig. IV-2

PHASE II TEST I ./25/65–2/7/65
HYDROGEN IN STEAM SAMPLE

NOTE:
SAMPLE POINT S-10
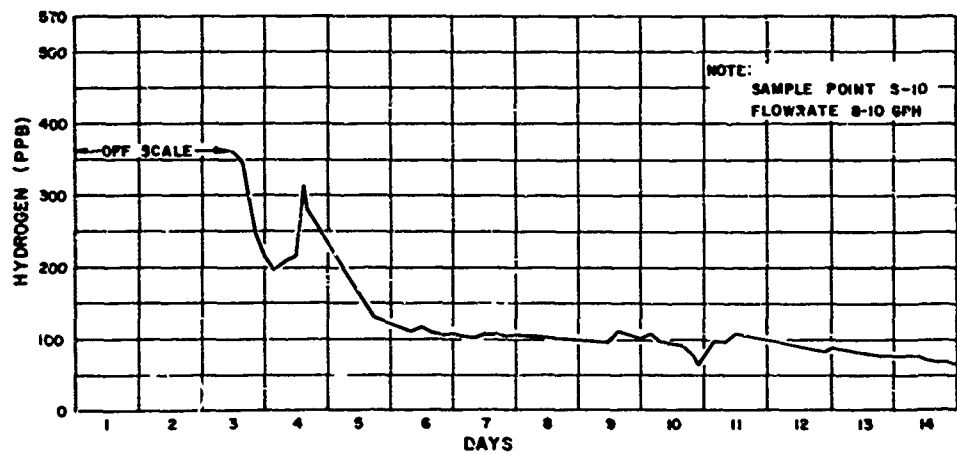FLOWRATE 8-10 GPH

OFF SCALE

Fig. IV-3

APPENDIX V

Log—Test 2, Phase II

Coordinated Phosphate Boiler Water Treatment
pH—9.8 to 10.0
Clean Boiler Conditions

Most water-chemistry specifications were easily maintained, although several days were spent reducing silica concentrations (Figs. V-1 and V-2). Hydrogen values were again initially high, but close to the end of the run reached lower steady-state conditions (Fig. V-3).

These levels indicated a heated surface corrosion rate of less than 1 mil per year.

Inspection of the test specimens revealed that the tubes were uniformly coated with iron oxide and that no corrosion had occurred. Deposit distribution and analysis are included in Table V-1. Metallurgical examination of the tube metal revealed no changes in structure.

TABLE V-1

TEST 2—PHASE II
(Phosphate Treatment—Clean Boiler)

DEPOSIT DISTRIBUTION

Loop	Q/A-Btu/hr-ft^2	Heated/Unheated Side	Block Location	Gm/Linear Ft.
A	110,000	Unheated	23	0.099
A	110,000	Unheated	22	0.088
A	110,000	Unheated	21	0.086
A	110,000	Heated	23	0.188
A	110,000	Heated	22	0.128
A	110,000	Heated	21	0.129
B	110,000	Unheated	24	0.096
B	110,000	Unheated	23	0.105
B	110,000	Unheated	22	0.117
B	110,000	Heated	24	0.134
B	110,000	Heated	23	0.153
B	110,000	Heated	22	0.154

DEPOSIT ANALYSIS

X-ray Diffraction
    Major, > 30%—Fe_3O_4
    Minor,   None
    Trace,   None

Spectrography
    Major, > 15%—Fe
    Minor,   None
    Trace, 0.1 to 1.0%—Ni, Mn, Si, Cr, Mg, Al, Mo, Cu, As

Wet Chemistry
    Na_2O—0.25%
    P_2O_5—<1.0%

PHASE Ⅱ TEST 2 3/23/65—4/5/65
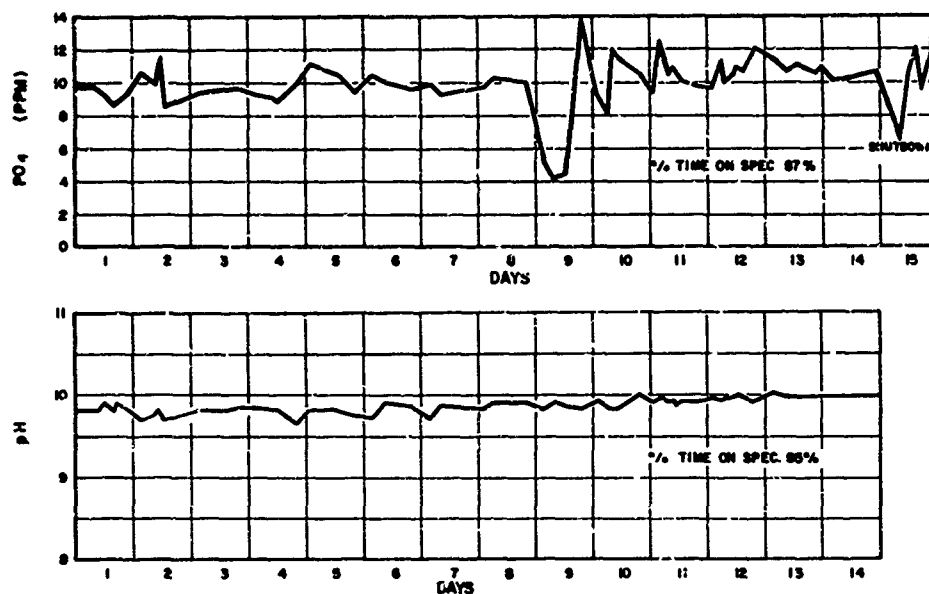### BOILERWATER CHEMISTRY

Fig. V-1

PHASE Ⅱ TEST 2 3/23/65-4/5/6C
BOILERWATER CONDUCTIVITY
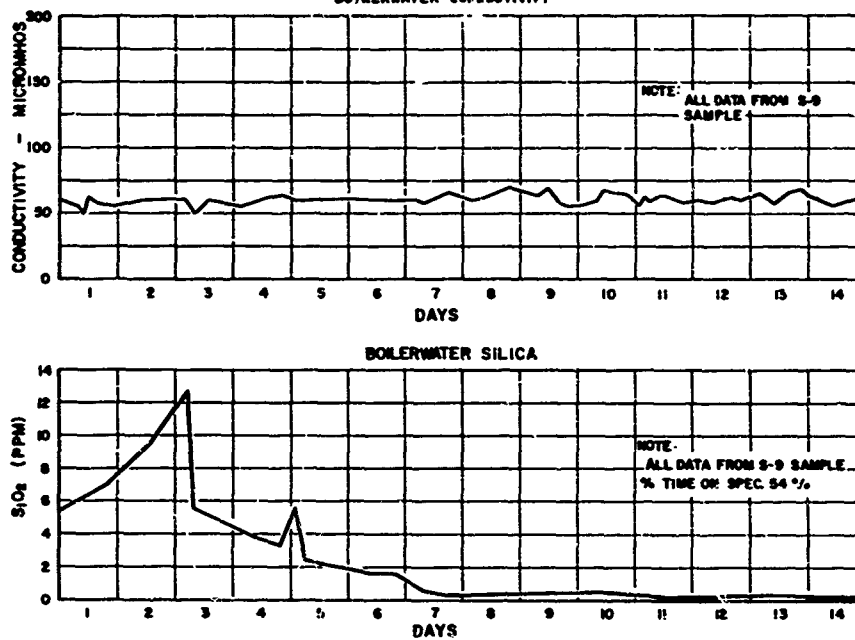
BOILERWATER SILICA

Fig. V-2

PHASE Ⅱ TEST 2 3/23/65-4/5/66
HYDROGEN IN STEAM SAMPLE
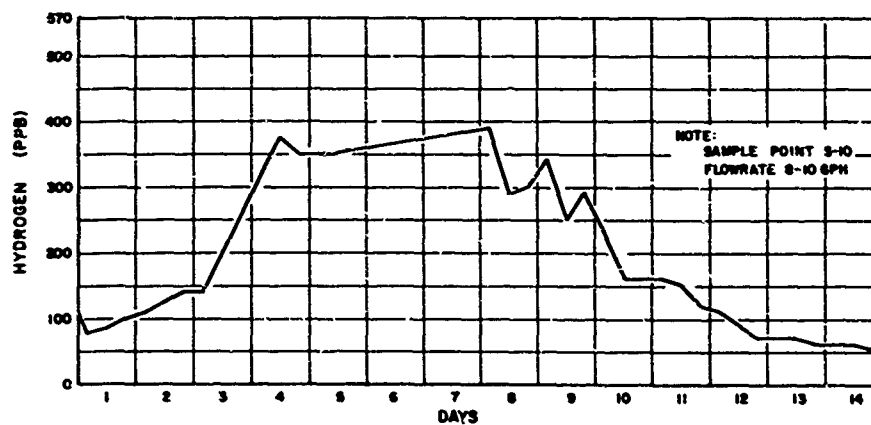
Fig. V-3

Caustic (NaOH) Boiler Water Treatment
pH = 10.5 to 10.7
PO_4 = 2 to 4 ppm
Clean Boiler Conditions

Boiler-water specifications were maintained to a maximum degree throughout the test. Silica problems were not so severe as during previous tests; however, hydrogen levels were excessively high.

After five days of operation with high hydrogen and occasional occurrences of "black water", a bearing failure in the circulating pump caused the test to be aborted. Upon shutdown to repair the circulating pump, it was decided that several equipment modifications should be made prior to re-running.

In order to eliminate silica contamination of the boiler water, an evaporator was incorporated into the system.

Hydrogen levels in excess of those of either the volatile or phosphate runs were experienced during this test. This appeared to be the result of corrosion due to steam blanketing in the low-velocity tube runs of the hori-

zontal-preheat furnace. Figure 11 shows the appearance of this corroded surface. The original pre-heater was, therefore, replaced.

A reflux condenser was installed to permit rapid blow-down of hydrogen from the boiler. This device allows the accumulation of non-condensibles at its upper portion, as the steam condenses on the walls, thereby eliminating the entrainment problem of the original condenser.

Subsequent to the repairs and modifications, this caustic test was rerun. The modifications resulted in lower hydrogen values and fewer problems in maintaining specified silica concentrations (Figs. VI-1 through VI-3). Steady-state hydrogen data indicated a heated surface corrosion rate of less than 1 mil per year.

Destructive examination of the test sections from the completed test revealed that no corrosion had occurred and that little deposit had accumulated on the test surfaces. Distribution and analysis of the deposits are included in Table VI-1. Metallurgical examination of the tube metal revealed no changes in structure.

TABLE VI-I

TEST 3—PHASE II
(Caustic Treatment—Clean Boiler)

DEPOSIT DISTRIBUTION

Loop	Q/A-Btu/hr-ft²	Heated/Unheated Side	Block Location	Gm/Linear Ft.
A	110,000	Unheated	24	0.072
A	110,000	Unheated	23	0.078
A	110,000	Unheated	22	0.023
A	110,000	Heated	24	0.072
A	110,000	Heated	23	0.078
A	110,000	Heated	22	0.110
B	110,000	Unheated	24	0.039
B	110,000	Unheated	23	0.037
B	110,000	Unheated	22	0.038
B	110,000	Heated	24	0.103
B	110,000	Heated	23	0.057
B	110,000	Heated	22	0.056

DEPOSIT ANALYSIS

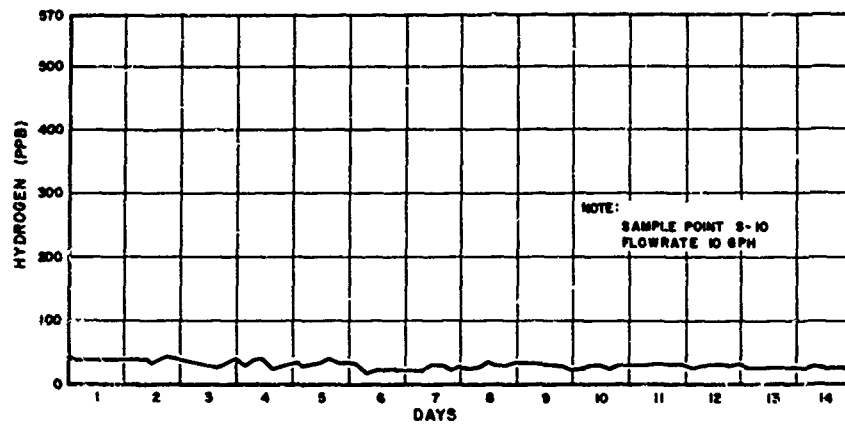|	
X-ray Diffraction	Major, > 30%—Fe_3O_4 Minor　　　None Trace　　　None
Spectrography	Major, > 15%—Fe Minor　　　None Trace, 0.1 to 1.0%—Ni, Mn, Si, Cr, Mg, Al, Cu
Wet Chemistry	Na_2O—0.2% P_2O_5—0%

PHASE II TEST 3 9/8/65 - 9/21/65

HYDROGEN IN STEAM SAMPLE

NOTE:
SAMPLE POINT S-10
FLOWRATE 10 GPH

Fig. VI-1

PHASE II TEST 3 9/8/65- 9/21/65

BOILERWATER CHEMISTRY

% TIME ON SPEC 94 %
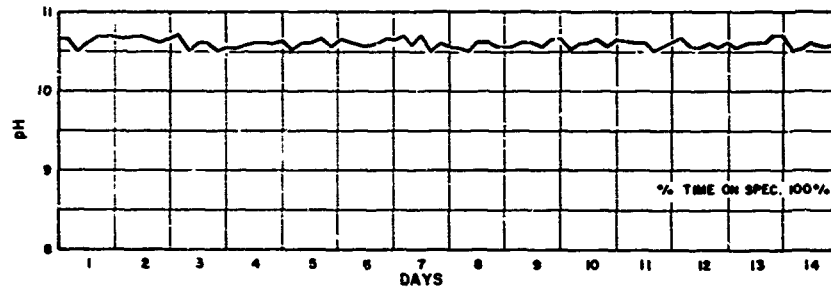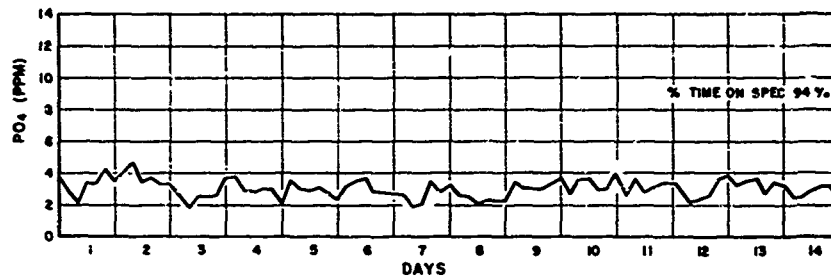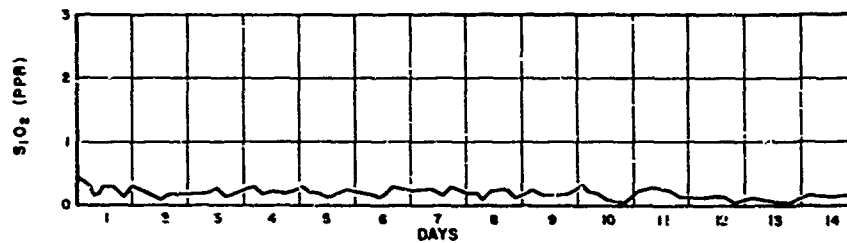
% TIME ON SPEC. 100%

Fig. VI-2

PHASE II TEST 3 9/8/65 -9/21/65

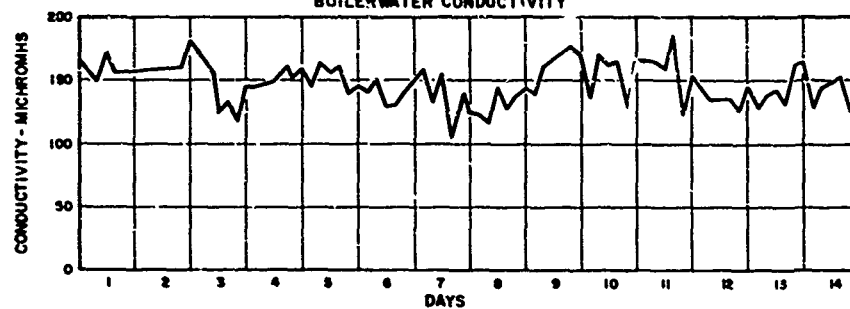**BOILERWATER SILICA**

BOILERWATER CONDUCTIVITY

Fig. VI-3

18

APPENDIX VII

Log—Test 1A, Phase III

Volatile (NH_3) Boiler Water Treatment
pH = 8.6 to 9.0
Dirty Boiler Conditions

At the beginning of this test, contaminants consisting of Fe_3O_4 and metallic copper powder were batch fed in the form of a slurry of 50 grams each at 2-hour intervals for several days. It had originally been proposed that these contaminants would be added until either (1) a 10-degree temperature rise was measured at the tube crown, or (2) a noticeable increase in pressure drop across the test section was experienced. Neither of these two phenomena occurred during initial operation. DNB was encountered at specified operating conditions shortly after the first introduction of contaminant. At this time it was necessary to reduce mixture quality by decreasing the preheat power, to avoid operation in the DNB region. Subsequent additions were made at 2-hour intervals throughout the first two days of the test. DNB occurred at less than the clean-tube critical-quality level during this period. This effect was temporary and after the critical quality again rose, approaching clean-tube values, additional contaminants were added. Further additions were guided by this phenomenon rather than either of the originally proposed factors. Neither a 10 F temperature rise nor a measurable change in pressure drop was noted during this test. Depression of critical quality thus became the limiting factor for all of the dirty-boiler runs.

Water chemistry specifications were easily maintained throughout the test (Figs. VII-1 through VII-3). On the 9th day of operation, the Northeastern power failure interrupted the test for an 8-hour period. The loop was returned to service immediately upon restoration of power, test conditions were re-established, and additional contaminants were added when it was found that the critical quality was back to the clean-tube level. The test was continued with the addition of contaminants throughout the remaining five days. Deposits resulted in 7-F temperature rise at the Block 20A tube-crown. (Block 20A experienced the greatest temperature increase in all tests and is used as a reference for purposes of comparison.)

Examination of the tube surfaces revealed that deposits, 2–6 mils thick, had formed on the heated tube surface. Analysis and distribution of these deposits are included in Table VII-1.

Portions of the test section beneath the heaviest deposits were chemically cleaned to examine the metal (Fig. VII-4). Faint traces of corrosion, in the form of general wastage and estimated to be no more than 0.1 mil, were noted along a band approximately 3/8 in. wide on the tube crown of the high-heat-flux section. Visual indications of corrosion consisted of discontinuities in the mandrel marks and scratches on the tube surface in this area.

After earlier tests, attempts had been made to mount and polish the deposits on tube specimens. These attempts met only with partial success; however, a technique using a highly fluid epoxy, which totally penetrated deposits, proved satisfactory. The use of this material resulted in a bone-hard mount which could be polished to reveal the deposit structure.

Photomicrographs (Fig. VII-5), at 100x and 400x, show the structure of the deposit from this run.

Analysis of the deposit revealed the presence of copper as well as large amounts of silica. The occurrence of Fe_2O_3 may be the result of the oxidation of some of the magnitite upon addition to the hot pressure pot or during loop shutdown. Examination of the metal structure revealed that no changes had occurred during this test.

Fig. VII-6 is a photograph of the recorder chart from the hydrogen analyzer with an inset from the Block 20 elevation tube-crown temperature recorder. This photograph illustrates the increase in hydrogen concentration resulting from contaminant addition. The inset shows the response of the tube-metal temperature to DNB, which in this case was encountered at normal operating quality as a result of the deposition of contaminants. A reduction in preheat power to reduce quality at Block 20 and remove it from DNB was required. No increases in hydrogen evolution were experienced during periods of DNB.

TABLE VII-I

TEST 1A—PHASE III
(Volatile Treatment—Dirty Boiler)

DEPOSIT DISTRIBUTION

Loop	Q/A-Btu/hr-ft²	Heated/Unheated Side	Block Location	Gm/Linear Ft.
A	110,000	Unheated	24	0.034
A	110,000	Unheated	22	0.023
A	110,000	Unheated	21	0.034
A	150,000	Unheated	19	0.023
A	150,000	Unheated	18	0.026
A	150,000	Unheated	17	0.012
A	110,000	Heated	24	0.137
A	110,000	Heated	22	0.169
A	110,000	Heated	21	0.115
A	150,000	Heated	19	0.567
A	150,000	Heated	18	0.297
A	150,000	Heated	17	0.116
B	150,000	Unheated	19	0.012
B	150,000	Unheated	18	0.016
B	150,000	Unheated	17	0.034
B	150,000	Heated	19	0.075
B	150,000	Heated	18	0.064
B	150,000	Heated	17	0.099

DEPOSIT ANALYSIS

X-ray Diffraction	Major, >30%—Outer Layer—Cu
	Inner Layer—Fe_2O_3
	Minor, 4 to 30%—Outer Layer—Fe_2O_3, Fe
	Inner Layer—Cu, Cu_2O, Fe_3O_4
	Trace, <4%—Outer Layer—Cu_2O, Fe_3O_4
	Inner Layer—$Fe_2O_3 \cdot H_2O$, Fe_3O_4, Cu_2O

Spectrography	Major, >15%—Fe, Cu	
	Minor,	None
	Trace,	0.1 to 1.0%—Al, Ni, Mn, Mo, Na, P, Si

Wet Chemistry	Blocks:	21A-24A	17A-20A	17B-20B	Inner Layer 19A
	Fe_3O_4, %	50	46	63	33
	Cu, %	24	16	30	5
	SiO_2, %	9	16	1	19

PHASE III TEST I 11/1/65 – 11/14/65

HYDROGEN IN STEAM SAMPLE

Fig. VII-1

20

PHASE III TEST I 11/1/65 – 11/14/66
BOILERWATER CHEMISTRY

NH₃ (PPM)

DAYS

pH

N.E. POWER FAILURE

% TIME ON SPEC 99 %

DAYS
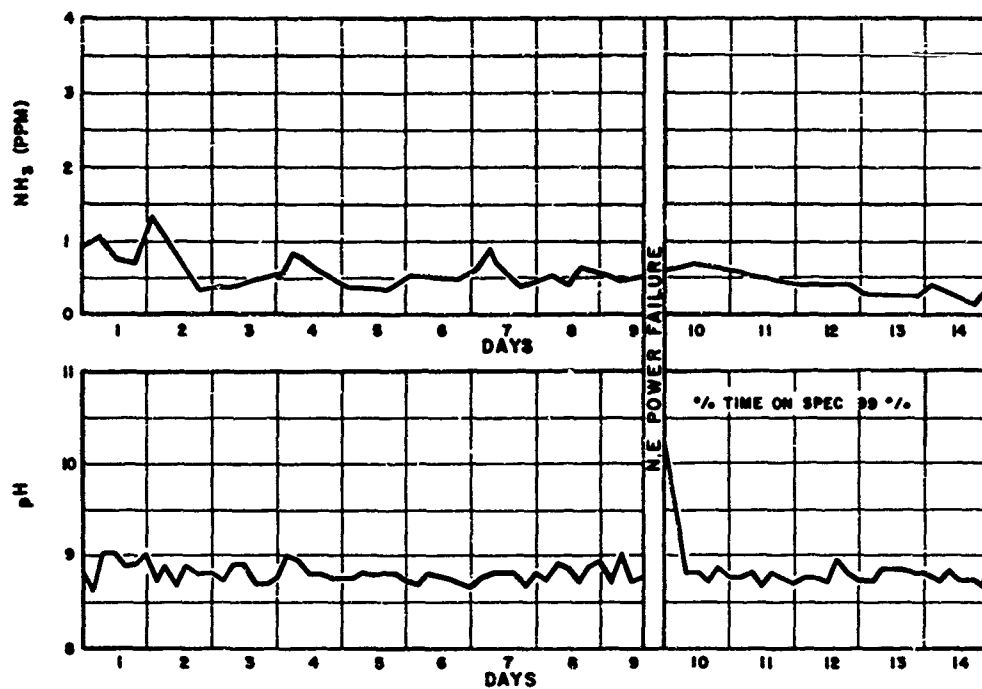
Fig. VII-2

PHASE III TEST I 11/1/65 – 11/14/65
BOILERWATER SILICA

S₁O₂ (PPB)

% TIME ON SPEC 100 %

N.E. POWER FAILURE

DAYS

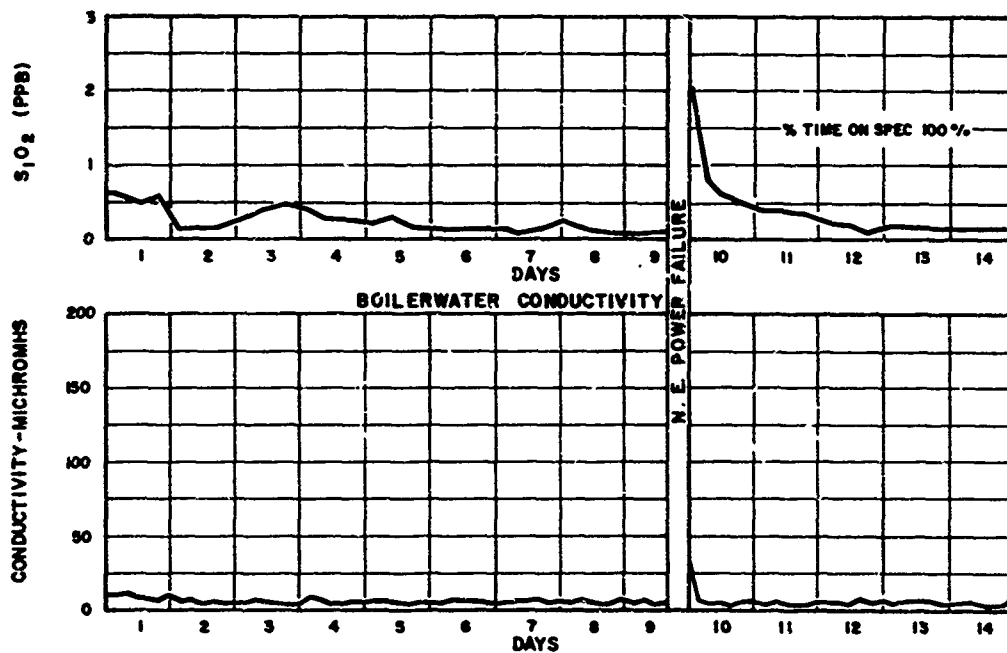### BOILERWATER CONDUCTIVITY

CONDUCTIVITY-MICROMHS

N.E. POWER FAILURE

DAYS

Fig. VII-3

19A

Fig. VII-4: Upper—Appearance of deposits formed on tube surfaces during the dirty boiler volatile test

Lower—Tube surface after removal of deposits by chemical cleaning

Fig. VII-6: Section of hydrogen analyzer recorder chart showing response to contaminant addition. S_1 is drum steam sample; S_{10} is reflux condenser sample. The inset of temperature recorder chart illustrates the instability in outside tube metal temperature resulting from DNB

Fig. VII-5: Upper—100x photomicrograph of the deposit cross section from the dirty boiler volatile test

Lower—400x photomicrograph as above

Coordinated Phosphate Boiler Water Treatment
pH = 9.8 to 10.0
Dirty Boiler Conditions

No problems in maintaining boiler water specifications were experienced (Figs. VIII-1 through VIII-3). Contaminant additions were made in a manner similar to the volatile treatment test. Similar reductions in critical quality to produce DNB were noted subsequent to the addition of these contaminants and their deposition on the test surfaces. No temperature rise or increase in test section pressure drop was seen during the run.

At completion of this test, the loop was shut down in sequence so that data relating to the amount and location of phosphate hideout could be obtained. Figure 12 is a plot of the phosphate contribution by the test surfaces to the boiler water upon shutdown. Initially, the decay in the boiler water phosphate concentration due to continuous sampling, was established and compared to the theoretical. Subsequent to this check, the phosphate level was increased to a point slightly above specified limits. Eliminating heat input to various test surfaces revealed that the lower "A" test section (blocks 17-20) had experienced considerable phosphate hideout.

Inspection of test surfaces after removal from the boiler showed considerable flaking off of the deposit. The amount of material from this run was approximately the same as from the volatile test (2 to 4 mils in thickness). No appreciable silica or copper was found in the deposits from this phosphate run (Table VIII-1).

A portion of the test section beneath the heaviest deposit was chemically cleaned so that the underlying metal surface could be inspected (Fig. VIII-4). Bands of very slight corrosion, estimated at no more than 0.1 mil, were noted approximately ½ in. apart along the tube crown of the high-heat-flux section. These bands correspond to the edges of the area where flaking had occurred. Visual effects of corrosion were apparent by discontinuities in the mandrel marks and scratches on the tube surface. Photomicrographs of the tube surface and cross section revealed the deposit to be extremely porous and raised from the tube in the area adjacent to where flaking had occurred (Fig. VIII-5).

Metallographic examination of the tube metal revealed no change in structure.

TABLE VIII-I

TEST 2A—PHASE III
(Phosphate Treatment—Dirty Boiler)

DEPOSIT DISTRIBUTION

Loop	Q/A-Btu/hr-ft²	Heated/Unheated Side	Block Location	Gm/Linear Ft.
A	150,000	Unheated	19	0.050
A	150,000	Unheated	18	0.052
A	150,000	Unheated	17	0.058
A	150,000	Heated	19	0.317
A	150,000	Heated	18	0.486
A	150,000	Heated	17	0.126
B	150,000	Unheated	19	0.017
B	150,000	Unheated	18	0.015
B	150,000	Unheated	17	0.012
B	150,000	Heated	19	0.128
B	150,000	Heated	18	0.120
B	150,000	Heated	17	0.121

DEPOSIT ANALYSIS

X-ray Diffraction	Major,> 30%—Fe_2O_3	Spectrography	Major,>%15%—Fe
	Minor, None		Minor, None
	Trace, <4.0%—Fe_3O.		Trace, 0.1 to 1.0%—Mn, Mg, Cu, Si, Ca
Note:	Cold side, Minor Cu detected	Note:	Cold side includes above plus Ni and Al

Wet Chemistry Fe_3O_4,% —94
Cu, % — 1.2
SiO_2, % — 0.5

PHASE II TEST 2 12/6/65−12/19/65
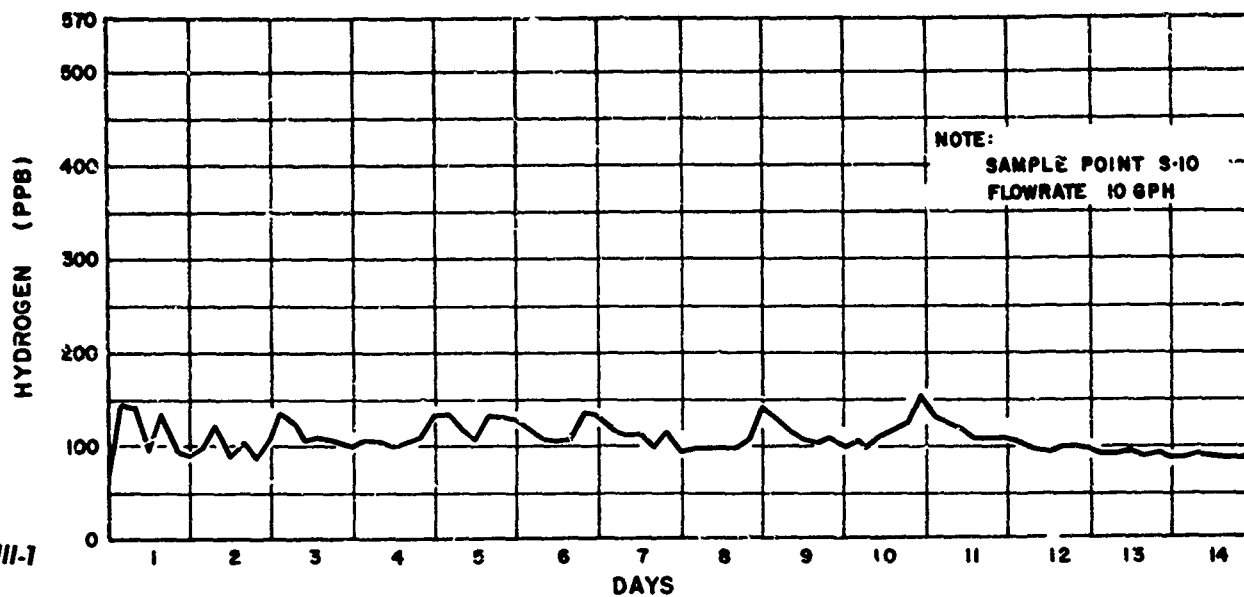
HYDROGEN IN STEAM SAMPLE

Fig. VIII-1

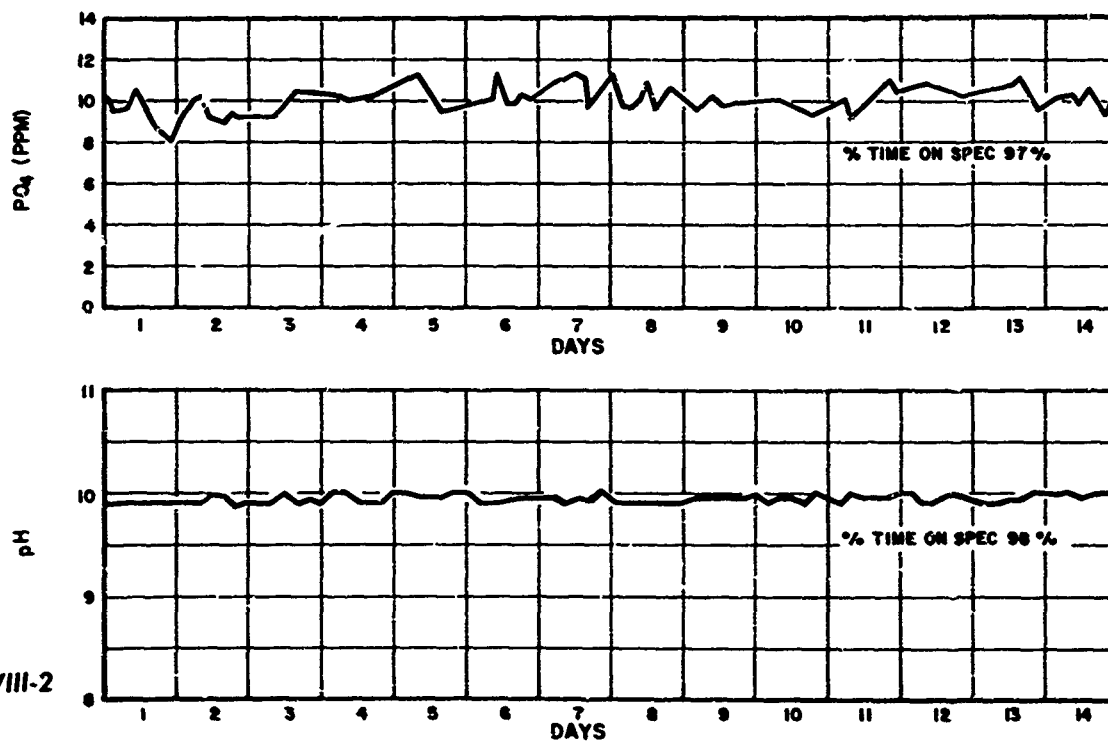PHASE II TEST 2 12/6/65 −12/19/65

BOILERWATER CHEMISTRY

Fig. VIII-2

BOILERWATER SILICA

% TIME ON SPEC: 99%

SiO₂ (PPB)

DAYS

BOILERWATER CONDUCTIVITY
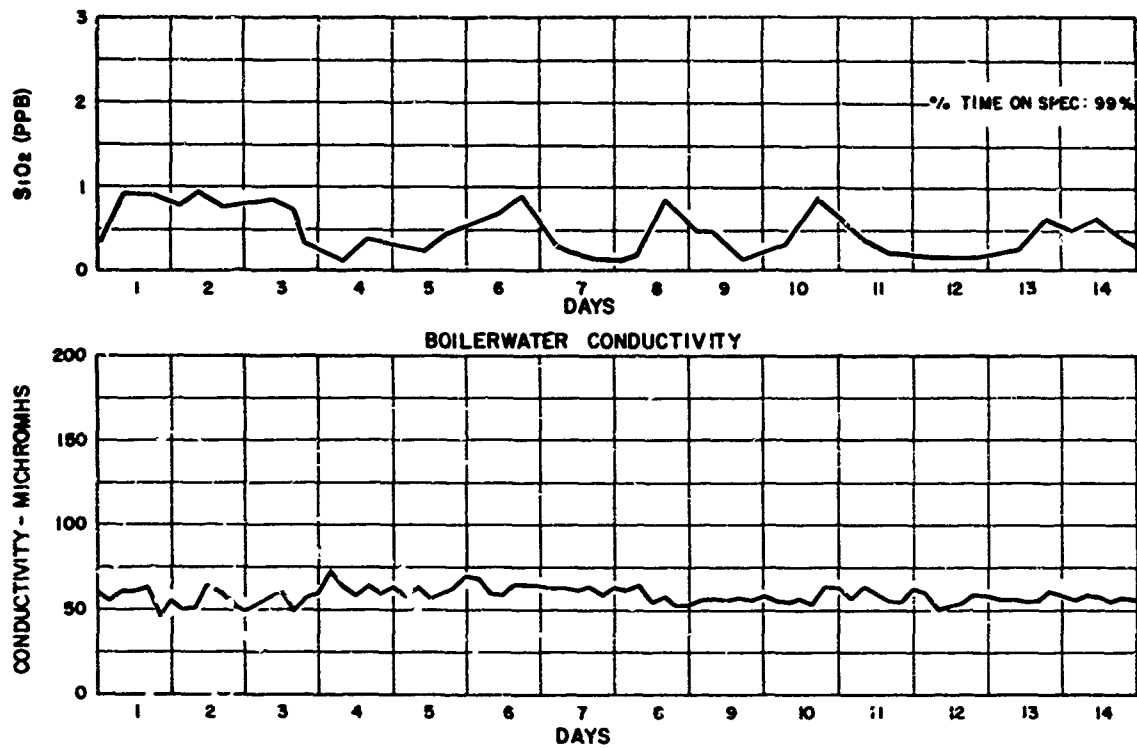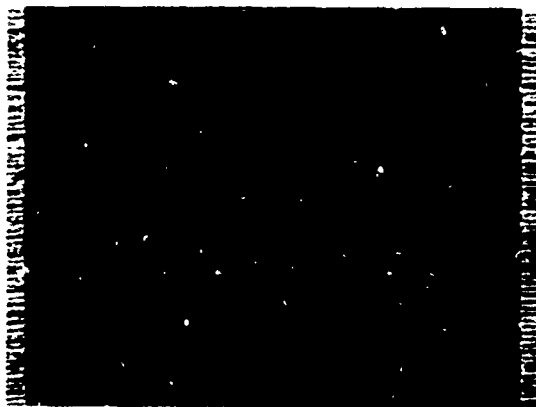
CONDUCTIVITY – MICHROMHS

DAYS

Fig. VIII-3

Fig. VIII-4: **Upper—Appearance of deposits formed on tube surfaces during the dirty boiler coordinated phosphate test**
Lower—Tube surface after removal of deposits by chemical cleaning.

Fig. VIII-5: **Upper—100x photomicrograph of the deposit cross section from the dirty boiler coordinated phosphate test**
Lower—400x photomicrograph as above

Caustic (NaOH) Boiler Water Treatment
pH = 10.5 to 10.7
PO₄ = 2 to 4 ppm
Dirty Boiler Conditions

Aborted Run

This test was run on a routine basis; however, 36 hours after the first addition of contaminant an instrument connection on the vertical-preheat tubing failed. As a result, the test was terminated at this time.

Within this period blocks 20A experienced a 25 F tube-crown temperature rise, which was three times the maximum temperature increase previously seen. Relatively high hydrogen concentrations had also been experienced during this period, so it was decided that the test sections should be removed from the loop for inspection. Borescope examination of the A test section revealed large amounts of deposit on the heated surface. This section was, therefore, retained for further examination. Since the B test section had much less deposit, it was acid cleaned and reinstalled. A new test section was fabricated and installed in the A loop.

In processing the A test section for analytical study, as much as 93 mils of deposit was found on the heated surface. Distribution and analysis of these deposits are included in Table IX-1. Examination of the chemically cleaned surfaces revealed corrosion in the form of a large number of small pits at the block 19 and 20 elevations. Figures IX-1 and IX-2 show the deposit formed and the corrosion which occurred during this 36-hour aborted run.

Completed Run

During this test contaminants were added in a manner similar to previous runs and boiler water chemistry was effectively maintained (Figs. IX-3 and IX-4).

Figure 7 illustrates the response of tube-crown temperature and hydrogen evolution to contaminant additions. It should be noted that even these initial levels greatly exceed the peak values experienced during previous tests. After 8 days of operation, a spontaneous increase in both temperature and hydrogen was noted. The rate of increase was accelerated when re-entrainment of deposits from the drum occurred due to flow oscillations induced by circulating pump cavitation resulting from a depressed water level. During this incident various portions of the test sections experienced DNB for a period of less than 10 minutes. This was not considered serious because no temperature excursion occurred, and test sections are often subjected to DNB

for periods of this length during critical quality tests. The first corrective action taken was to increase the flow rate to "wash out" DNB. The feedwater flow was then increased and the drum water level returned to normal.

After the particulate matter in the bulk fluid had redeposited, extremely high tube temperature and hydrogen concentrations were apparent. A spontaneous acceleration in tube temperature and hydrogen evolution was seen again on the 9th day. The severity of this rise was such that the test section appeared to be in danger of overheating, and hydrogen evolution beyond the range of the analyzer indicated gross attack of the tube metal. In order to regain control of both temperature and hydrogen evolution, the heat flux at the affected sections was reduced from 150,000 to 140,000 Btu/hr-ft². Temperature and hydrogen remained high until the test was terminated by a tube failure resulting from complete corrosion penetration of the tube at block 20 in the "A" test loop. Figures 8, 9, and IX-5 show the appearance of the loop, the ruptured tube, and the corrosion that occurred at Block 19 elevation.

Temperature rise and hydrogen evolution curves have been prepared showing comparative values from the aborted and completed caustic tests (Fig. 10). The duplication of general response shown by these curves indicates a similarity in the initiation of corrosion by the accumulation of contaminant materials on the test surfaces.

These data indicate that attack began immediately after the accumulation of deposit and bore a direct relationship to the temperature rise resulting from this accumulation. Hydrogen levels indicate that most of the corrosion took place during the last four days of operation.

In addition to the large temperature increases, a reduction in critical quality similar to previous runs was noted. Examination of the test sections revealed that corrosion in varying degrees had occurred at virtually all areas of the heated A and B test surfaces. The area most severely affected was at Block 20 in the "A" loop; however, Block 19 showed considerable penetration. What constituted minor pitting was noted throughout the balance of the test surface. As previously noted, similar pitting was found on the surfaces in the high heat flux area of the 36-hour, aborted-run, test sections. Metallurgical examination of representative specimens revealed no changes in metal structure.

As a result of the tube failure, virtually all of the deposits that had accumulated on the tubes were lost.

TABLE IX-I

TEST 3A—PHASE III
(Caustic Treatment—Dirty Boiler)

DEPOSIT DISTRIBUTION

Loop (Aborted Run)	Q/A-Btu/hr-ft²	Heated/Unheated Side	Block Location	Gm/Linear Ft.
A	150,000	Heated	20	1.560
A	150,000	Heated	19	0.716
A	150,000	Heated	18	0.388
A	150,000	Heated	17	0.300

DEPOSIT ANALYSIS

X-ray Diffraction	Major, > 30%—Fe_3O_4 High Minor, 15 to 20%—Cu Low Minor, 4 to 8%—Fe_2O_3
Spectrography	Major, > 15%—Fe, Cu Qualitative —P. Si. Na

Wet Chemistry
SO_3, %—None
CO_2, %—1-3
P_2O_5, %—6
SiO_2, %—1
Fe_3O_4, %—64
Na_2O, %—8
Cu, %—19
Total Ignition Loss, %—3
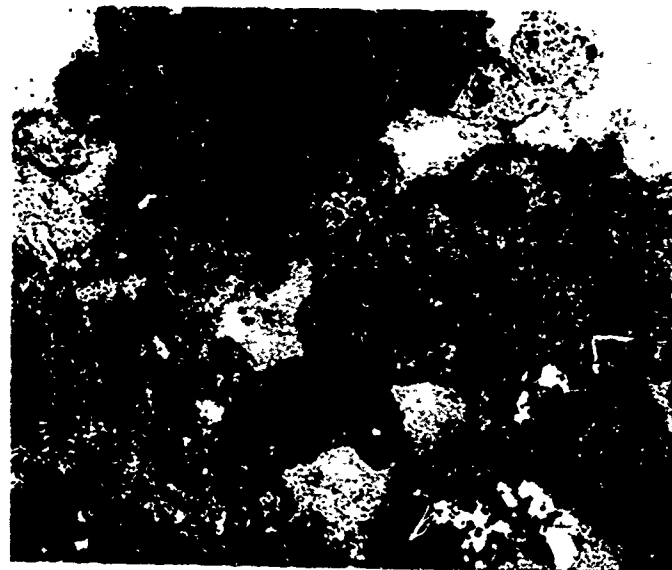
Fig. IX-1: Upper—Appearance of deposits formed on tube surfaces during the dirty boiler aborted caustic test

Lower—Tube surface after removal of deposits by chemical cleaning

Fig. IX-2: Upper and Lower—400x photomicrograph of the deposit cross section from the dirty boiler aborted caustic test

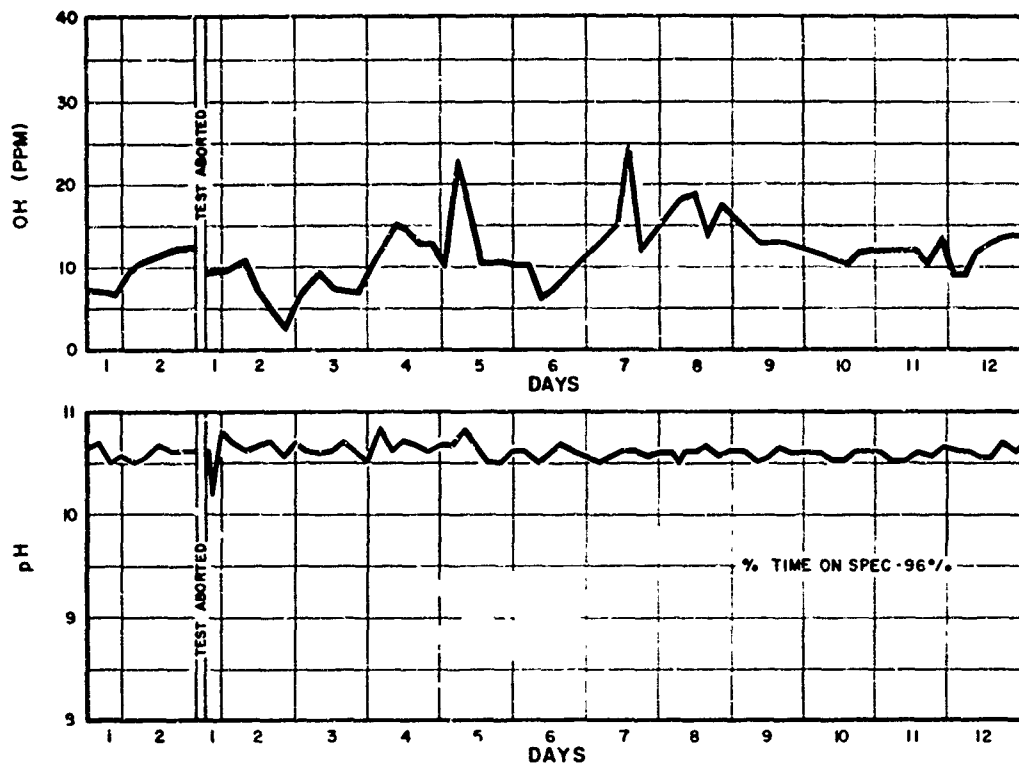PHASE III TEST 3 1/23/66 - 1/25/66, 1/27/66 - 2/8/66

BOILERWATER CHEMISTRY

Fig. IX-3

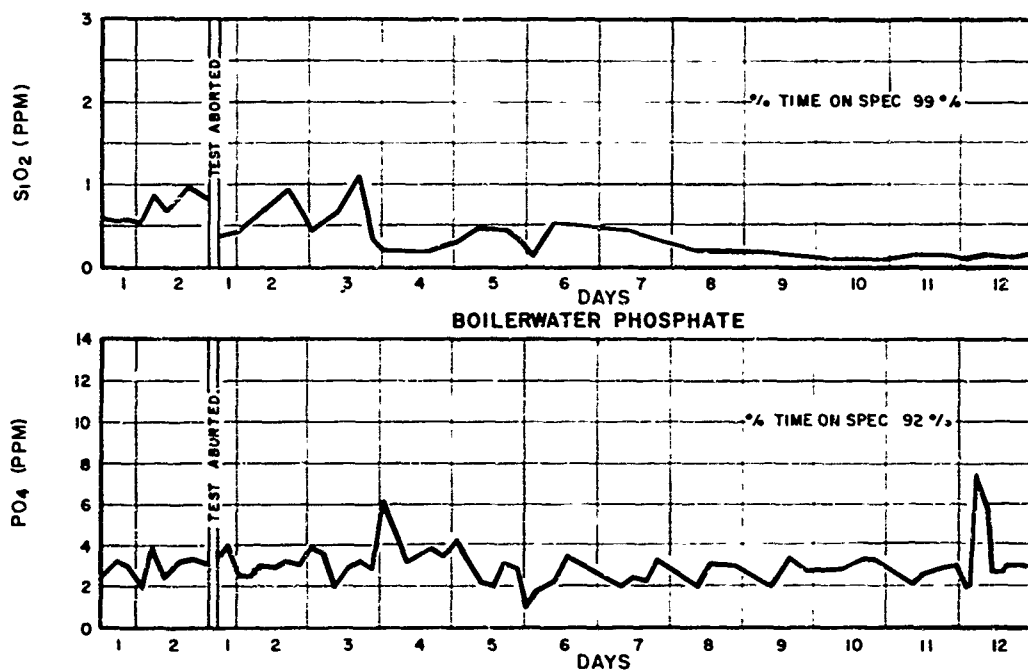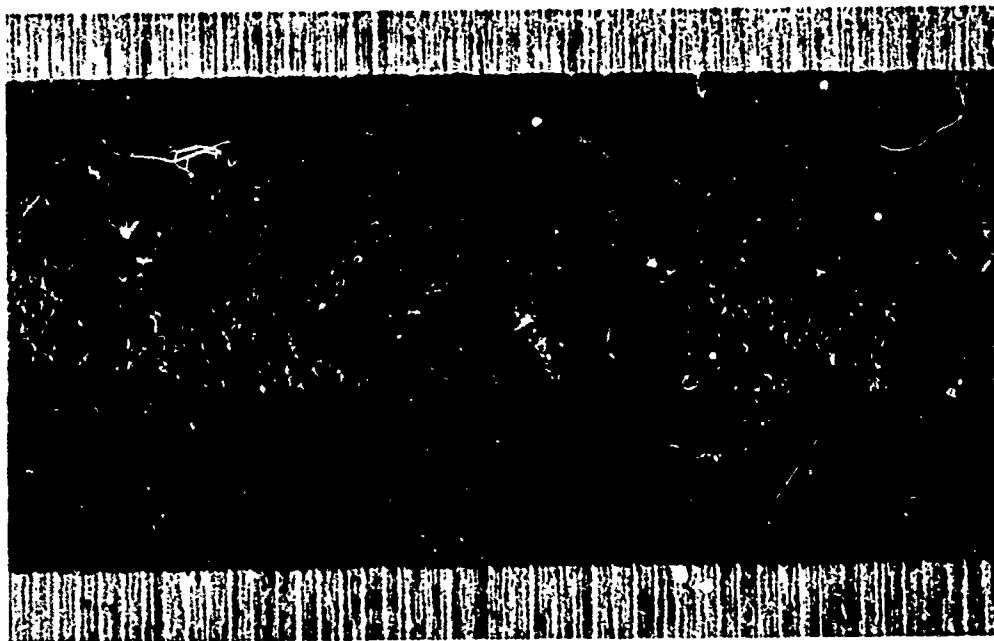PHASE III TEST 3, 1/23/66 - 1/25/66 , 1/27/66-2/8/66

BOILERWATER SILICA

BOILERWATER PHOSPHATE

Fig.. IX-4

Fig. IX-5: *Photograph showing corrosion at block 19A (1 ft. below the failure) from the dirty boiler caustic test*